Supporting information for "Dodecahedral W@WC composite as efficient catalyst for hydrogen evolution and Nitrobenzene reduction reactions"

Supporting Information

Dodecahedral W@WC Composite as Efficient Catalyst for Hydrogen Evolution and Nitrobenzene Reduction Reactions

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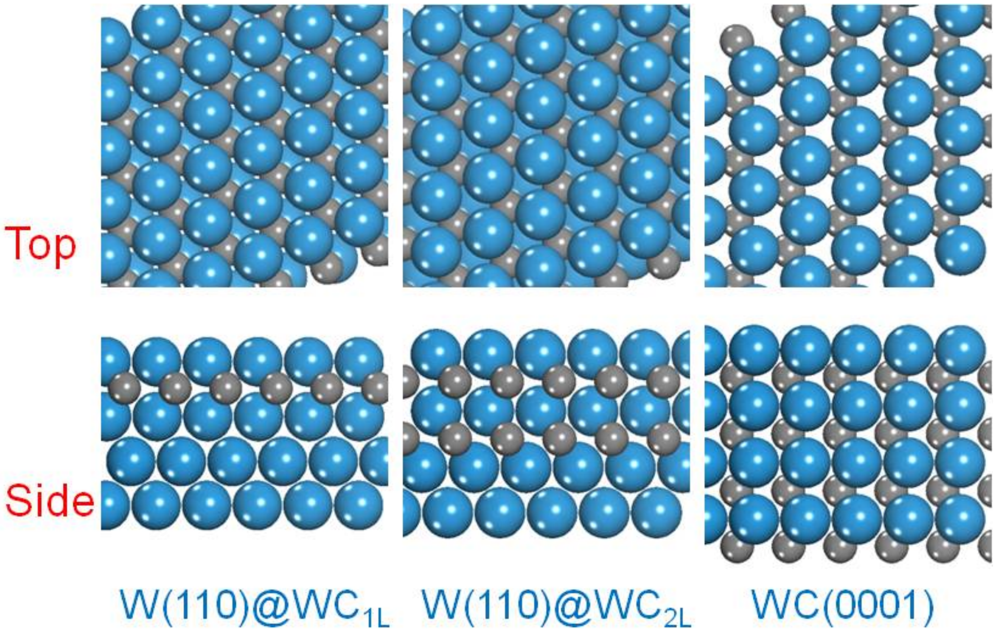


Figure S1. Top and side views of W(100)@WC_{1L} [one layer of WC on W(100)], W(100)@WC_{2L} [two layers of WC on W(100)] and WC(0001) models used in the DFT calculations. Cyan: W, grey: C.

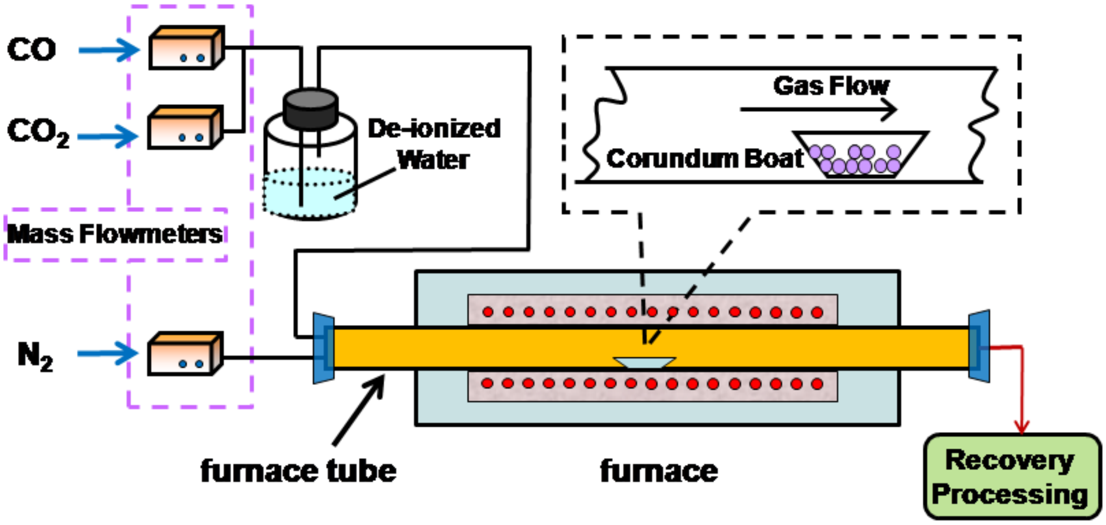


Figure S2. Schematic diagram of the setup used for the synthesis of W@WC.

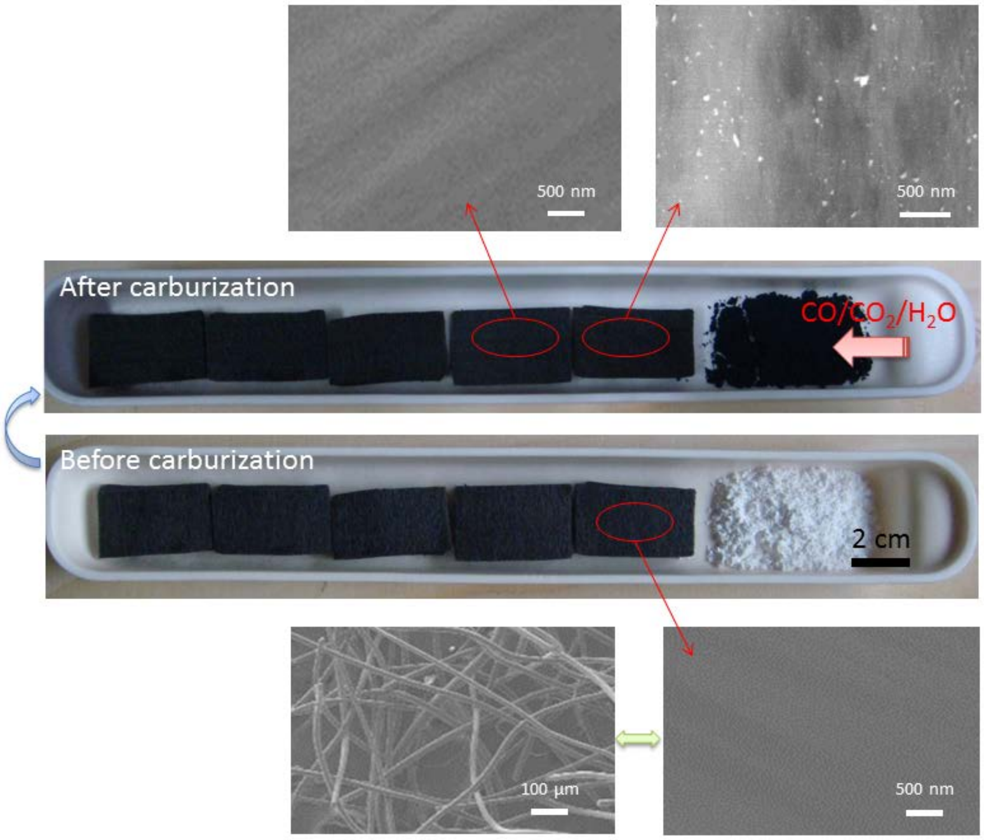


Figure S3. Photos showing the arrangements of the carbon felts used to testify the moving feature of gaseous $WO_2(OH)_2$, and the SEM images of the carbon felt surfaces before and after the carburation of the sample. Carbon felt was used to testify the moving feature of gaseous $WO_2(OH)_2$. In this process, $WO_2(OH)_2$ could be collected, and then be reduced by reductive gas around the carbon felt, which was placed close to the sample with the distance less than 4 cm. The collected moving mass of W was evidenced by the SEM images, showing a noticeable amount of W nanoparticles on the surface of the first carbon felt placed closest to the sample.

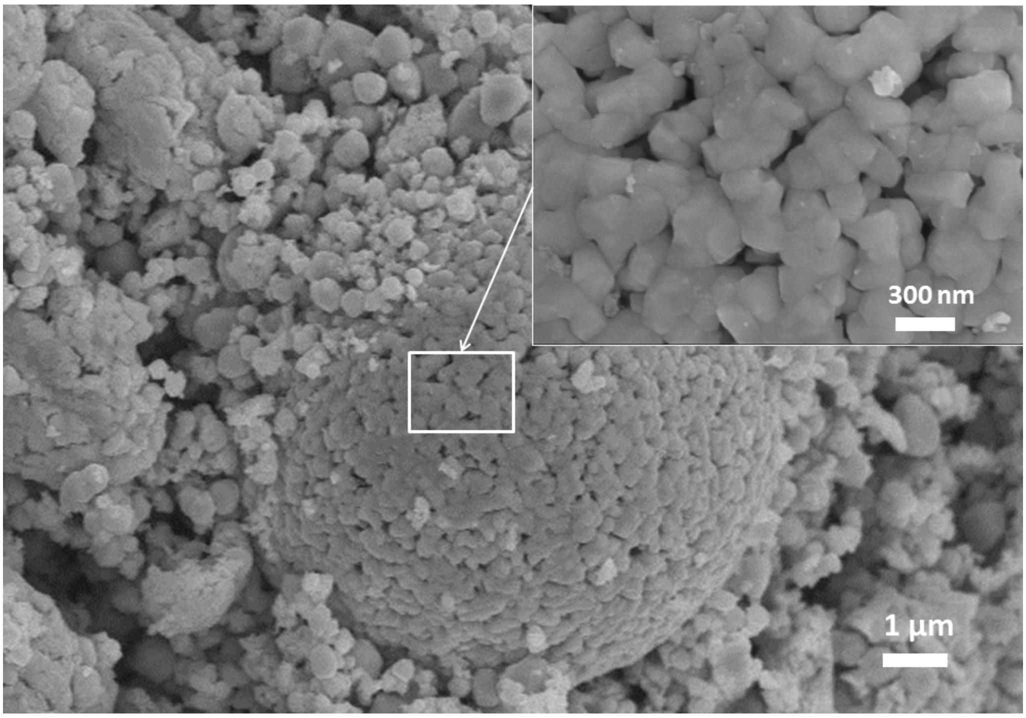


Figure S4. SEM images of the sample reduced under pure and dry H_2 gas at 850 °C for 12 h.

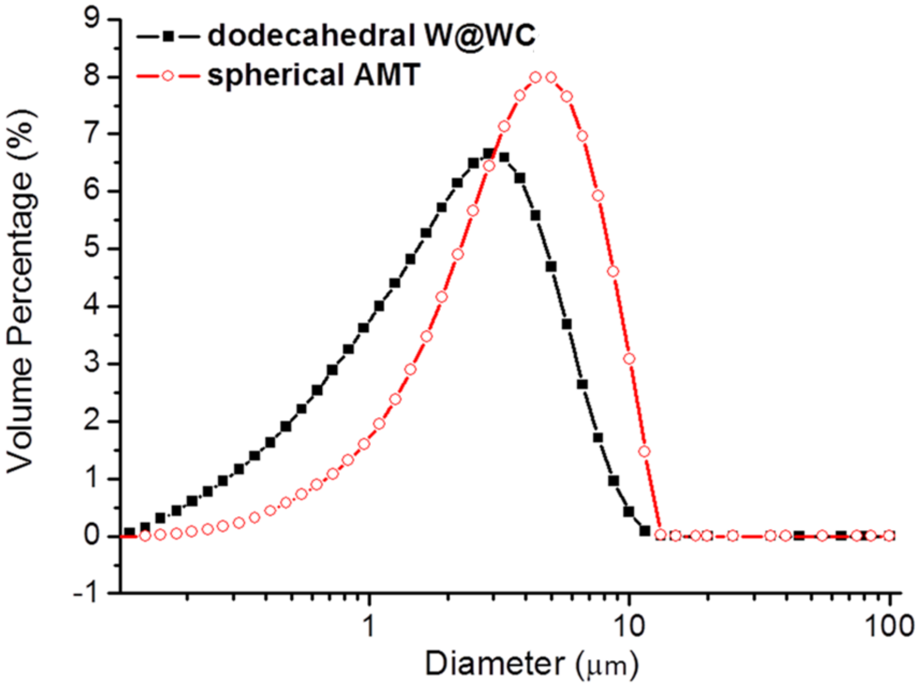


Figure S5. Particle size distribution of the spherical AMT precursor and the dodecahedral W@WC product.

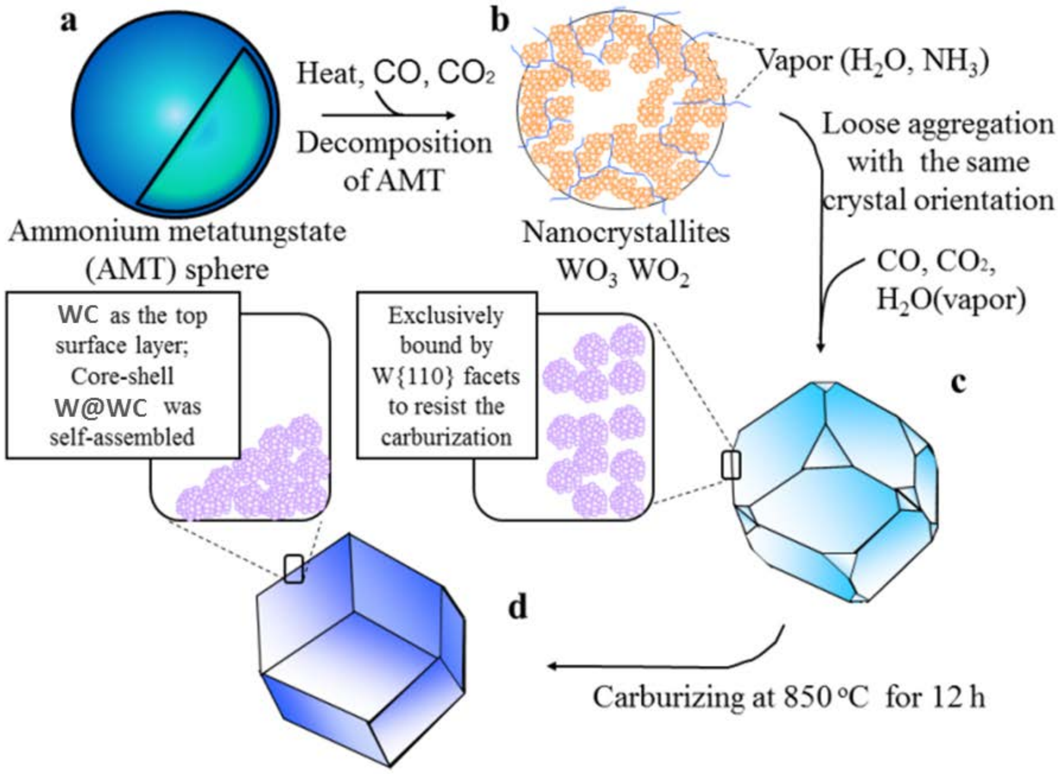


Figure S6. (a) AMT balls prepared by spray drying; (b) decomposition of AMT; (c) self-assembly of microboulder; (d) W@WC with dodecahedral microstructure.

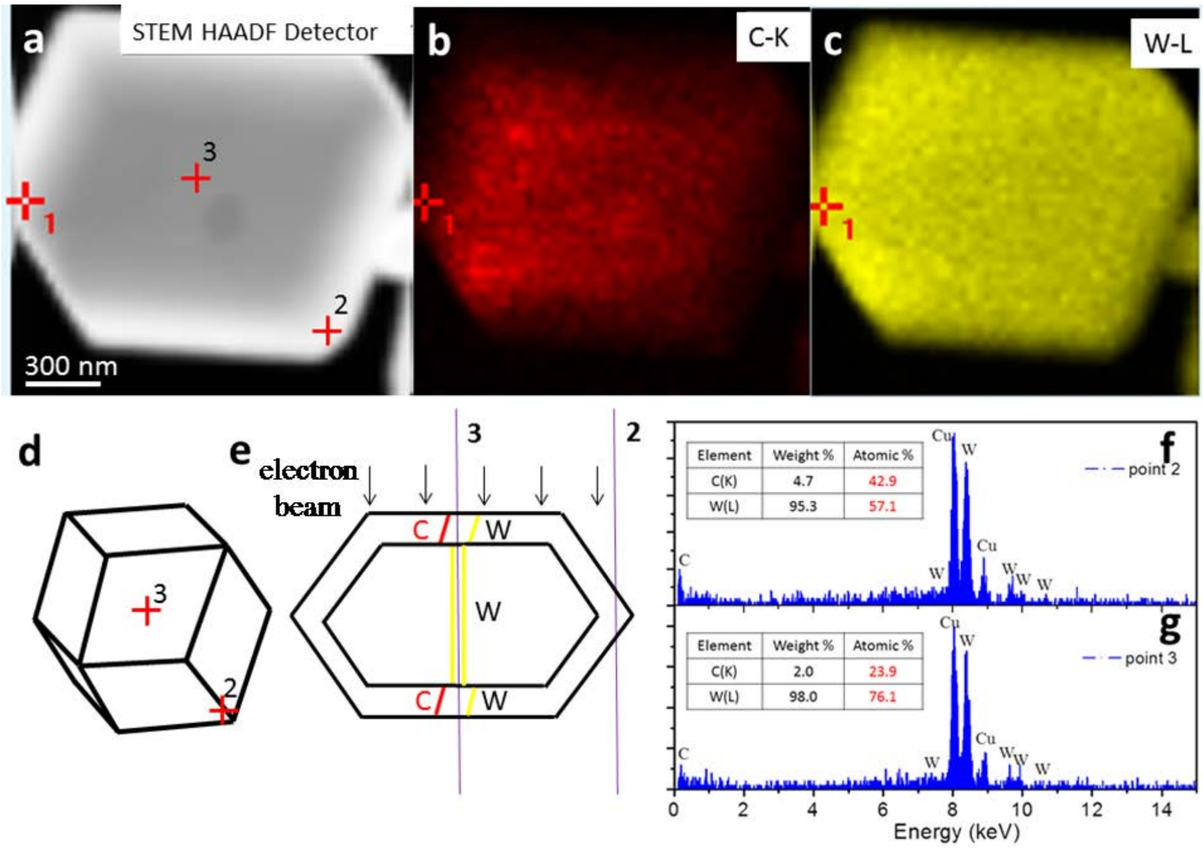


Figure S7. (a) STEM imaging and (b, c) simultaneous 2D STEM-EDS mapping from a representative W@WC; (d, e) Schematic diagram for the point 2 and 3; (f, g) the chemical components of the point 2 and 3 according to the EDS spectra. The EDS taken on the edges (e.g., point 2; serving as a probe for the shell) of a particle, shows that W:C atomic ratio is close to 1:1, whilst that taken on the middle (e.g., point 3, serving as a probe for the whole of shell and core) of a face of the particle showing a significant higher W:C ratio of ~3:1.

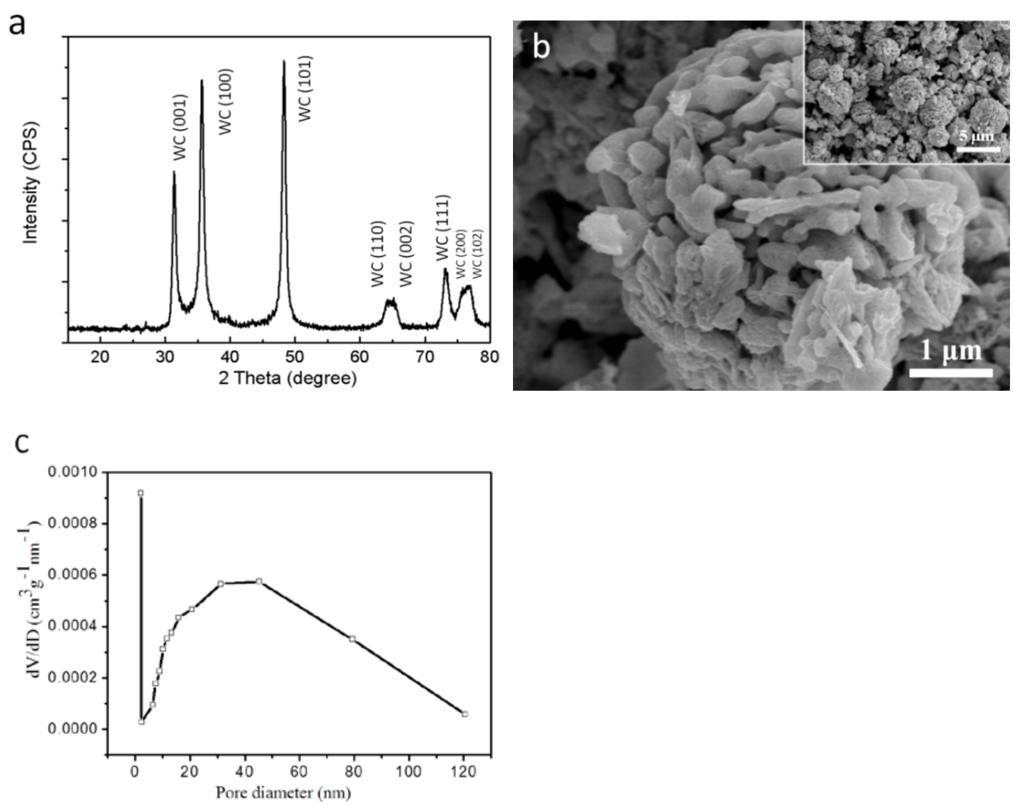


Figure S8. a) XRD pattern, b) SEM image and c) pore size distribution of a reference sample synthesized by carburizing the spray dried AMT with a dry CO/CO_2 mixture.

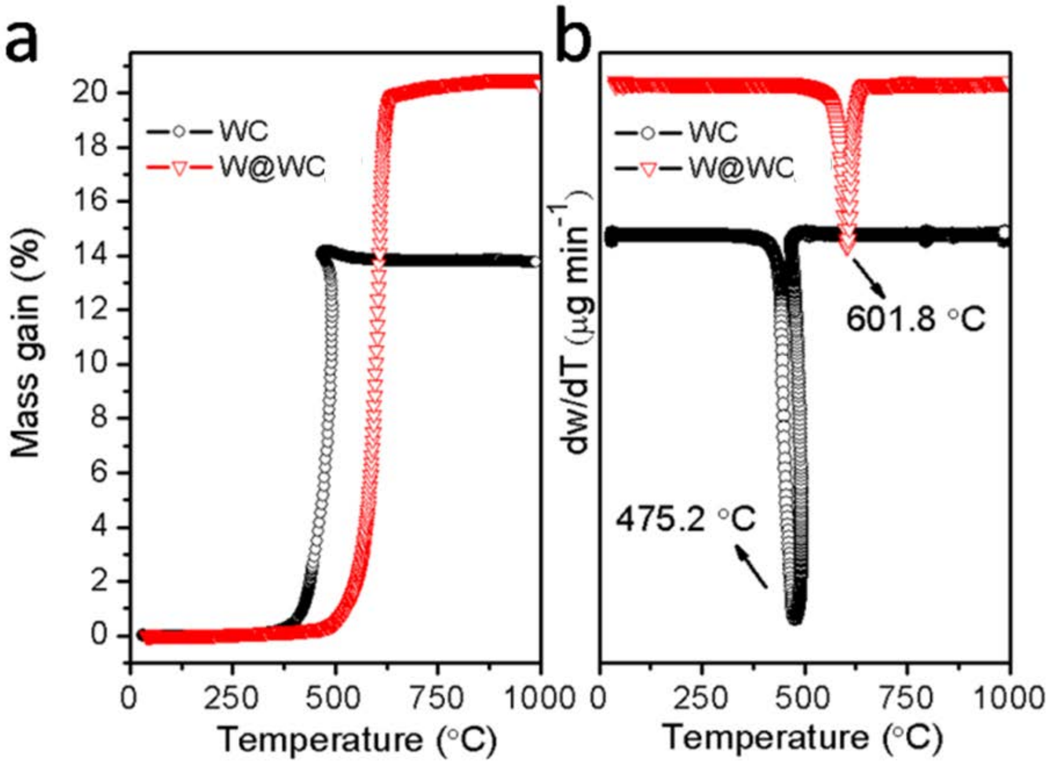


Figure S9. (a) Thermogravimetric curves, and (b) the corresponding derivative thermogravimetric curves for the W@WC and WC samples.

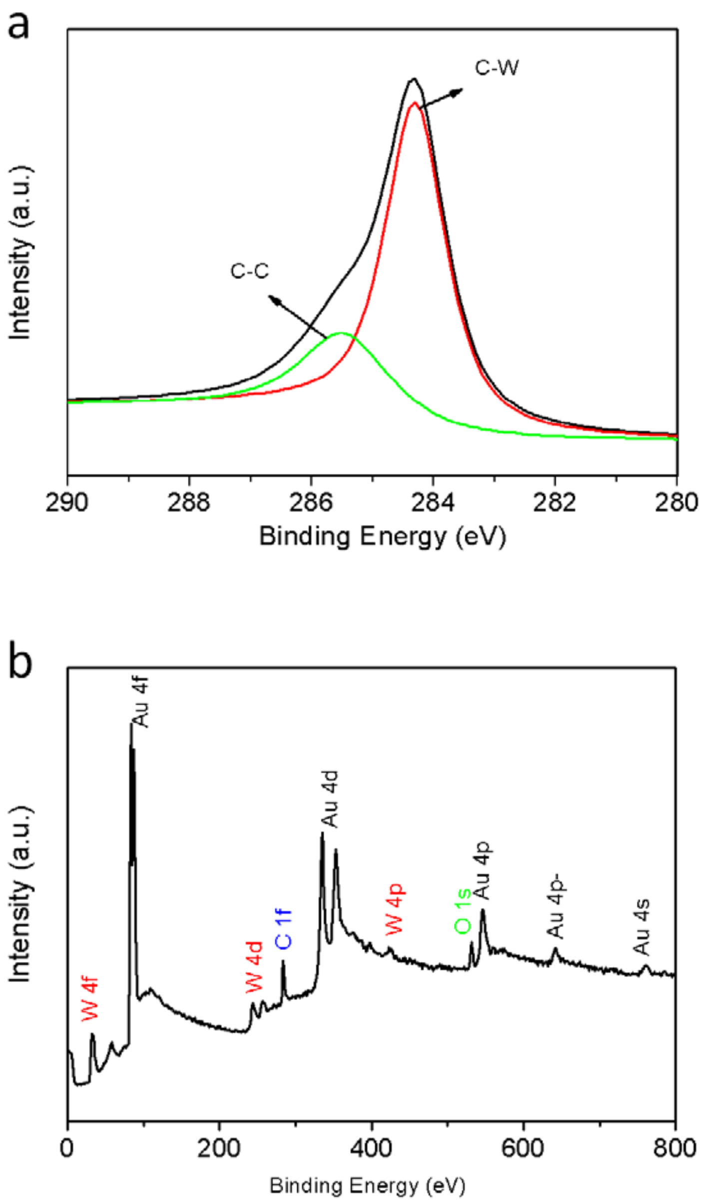


Figure S10. XPS spectra of the W@WC sample showing (a) C 1s and (b) Survey scan. In (b), the Au features are due to the fact that Au spraying was applied to the sample surface before the XPS measurements; Au $4f_{7/2}$ (84.0 eV) was chosen as the reference line.

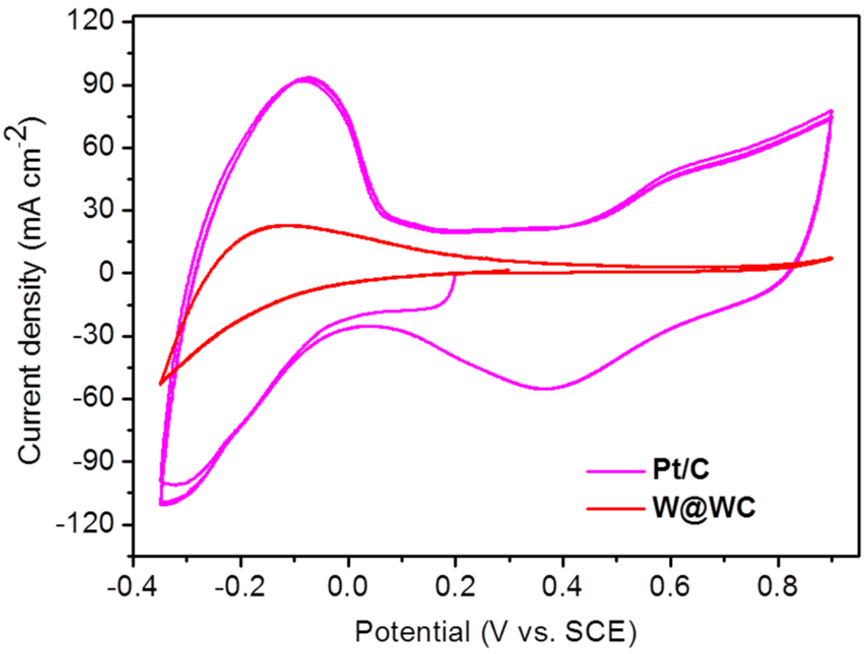


Figure S11. Cyclic voltammograms (CVs) of the W@WC and Pt/C in 0.1 $HClO_4$ supporting electrolyte solution; scan rate is 50 mVs^{-1}.

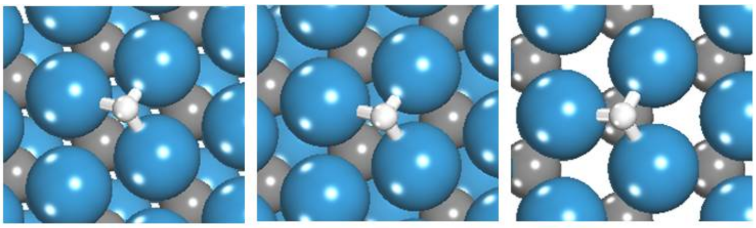


Figure S12. Optimized structures of hydrogen adsorption on W(110)@WC_{1L},W(110)@WC_{2L} and WC(0001) surfaces. Cyan: W, grey: C, white: H.

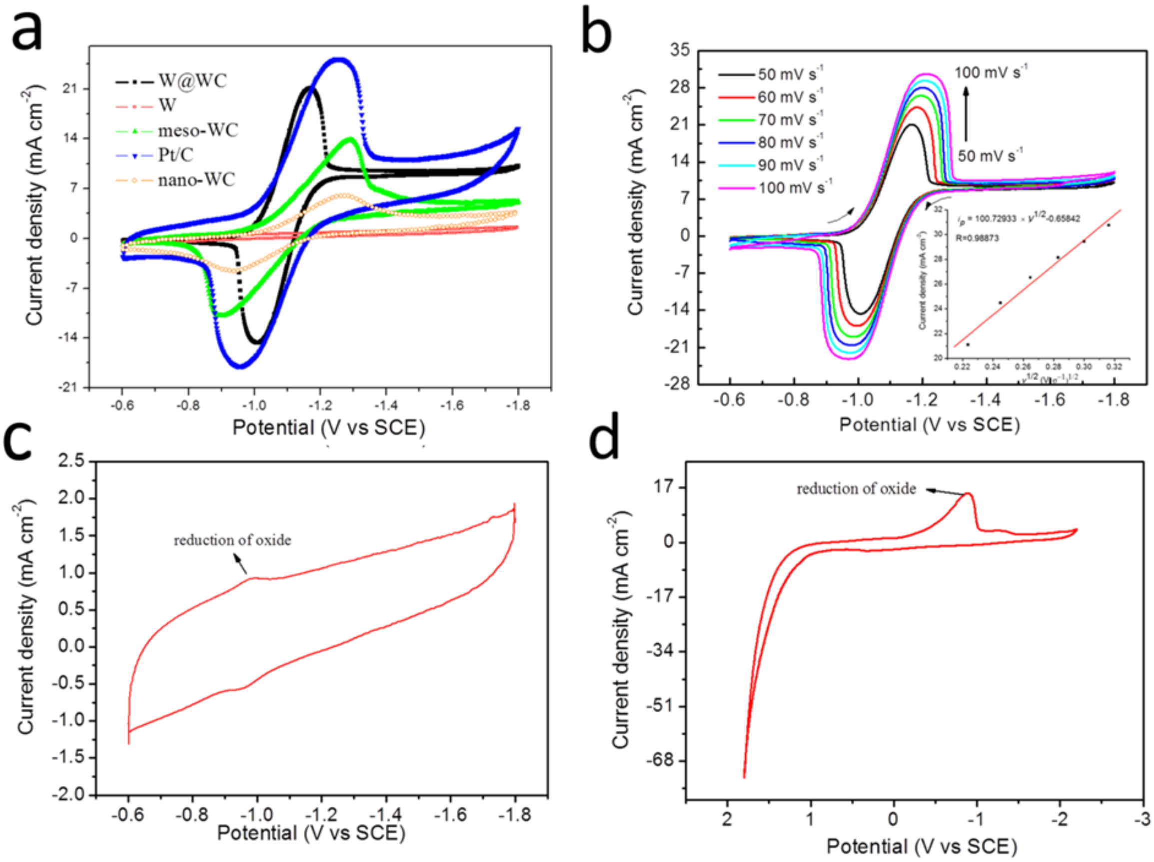


Figure S13. a) Cyclic voltammograms (CVs) of W@WC, meso-WC, nano-WC, W and a Pt/C in 0.1M TBAP DMF solution containing 0.03 M nitrobenzene, the scan rate is 50 mVs^{-1}. **b)** CVs of the prepared W@WC in 0.1M TBAP DMF solution containing 0.03 M nitrobenzene with different scan rates (ν), the inset shows relationship between $\nu^{1/2}$ and the cathodic peak current density. The NB electrochemical reduction process on the W@WC is evidenced to have the liquid-phase mass transfer as the limiting factor but not adsorption and surface reaction, thanks to the high activity of the W@WC electrode. **c)** Cyclic voltammogram (CV) of the as prepared W@WC sample in 0.1 M TBAP DMF supporting electrolyte solution. **d)** CV of the calcined W@WC in supporting electrolyte 0.1 M TBAP DMF solution.

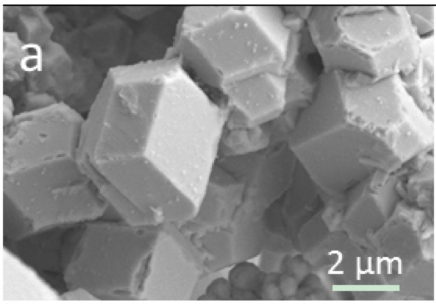
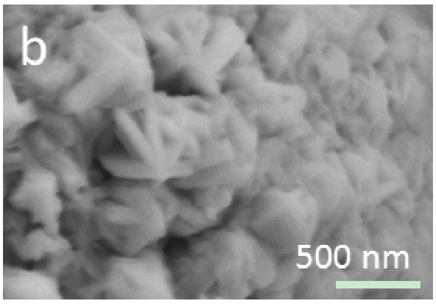
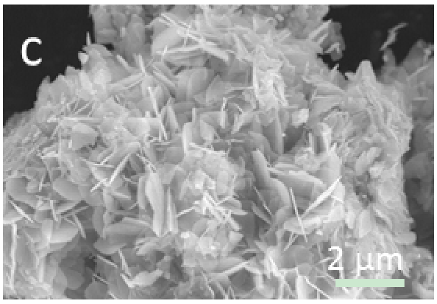
Morphology	Synthesis conditions	Component
	**Gas: CO/CO_2** **Temperature: 850 ℃** **H_2O mediated**	**MoC(Mo)**
	**Gas: CO/H_2** **Temperature: 800 ℃** **H_2O mediated**	**W_2C**
	**Gas: CO/H_2** **Temperature: 800 ℃** **H_2O mediated**	**Al**

Figure S14. SEM images of the other carbides and metal samples obtained by using a similar synthesis process as reported here; (a) MoC(Mo), (b) W_2C and (c) Al.